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Oxidative torrefaction of biomass residues and densification of torrefied sawdust to pellets

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HIGHLIGHTS

- ▶ An oxidation torrefaction kinetics model was developed based on TGA data.
- ▶ Sawdust was torrefied in a fluidized bed reactor using oxygen-laden combustion flue gases.
- ▶ Torrefied sawdust was compressed into pellets of properties similar to regular pellets.

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ABSTRACT

Oxidative torrefaction of sawdust with a carrier gas containing 3–6% O_2 was investigated in a TG and a fluidized bed reactor, with the properties of the torrefied sawdust and pellets compared with traditional torrefaction without any O_2, as well as the dry raw material. It is found that the oxidative torrefaction process produced torrefied sawdust and pellets of similar properties as normally torrefied sawdust and corresponding pellets, especially on the density, energy consumption for pelletization, higher heating value and energy yield. For moisture absorption and hardness of the torrefied pellets, the oxidative torrefaction process showed slightly poor but negligible performance. Therefore, it is feasible to use oxygen laden combustion flue gases as the carrier gas for torrefaction of biomass. Besides, torrefied sawdust can be made into dense and strong pellets of high hydrophobicity at a higher die temperature than normally used in the production of traditional control pellets.

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1. Introduction

Currently, the interest in developing renewable energy has received considerable attention. Among these renewable energies, the unique position of biomass as the only renewable source as a sustainable carbon carrier makes biomass an attractive energy source (Pa et al., 2011). However, structural heterogeneity, non-uniform physical properties, low energy density, high moisture content and a hydrophilic nature of biomass have become major problems in its efficient and economic transport, handling, storage and conversion into bioenergy products (Lam et al., 2012). In order to address the above problems, biomass needs to be pretreated or upgraded in order to improve its quality for efficient energy conversion (Stelt et al., 2011; Uslu et al., 2008).

Torrefaction is a mild pyrolysis of biomass at temperatures between 200 and 300 °C, normally in the absence of oxygen (Chen et al., 2011b; Medic et al., 2012). During torrefaction of biomass, considerable increase in energy density is achieved, whilst its fuel properties are improved to yield a fuel of much better quality for combustion and gasification applications (Chen et al., 2011a; Prins et al., 2006). The grindability is also improved by torrefaction to enable more efficient co-firing in existing pulverized coal power plants or entrained-flow gasifiers for the syngas production (Bergman et al., 2005b; Phanphanich and Mani, 2011). In combination with pelletization, torrefaction also aids in addressing the logistic issues for untreated biomass pellets, such as low energy density and low hydrophobicity. Torrefied pellets can potentially reduce the handling costs and result in a solid fuel of standardized shape and size that can be fed automatically to solids-fuel boilers for heat and power generation (Bergman, 2005a). As a result, there

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is a strong interest in utilising torrefied wood pellets in existing large-scale combined heat and power (CHP) plants to replace coal with a biofuel without major changes in the power plant design (Bergman et al., 2005c). Biomass composition has a great effect on the pellet quality and the pelletizing process itself, and many researches have been focused on the production of biomass pellets produced from mixtures of different agricultural and forestry residues (Gil et al., 2010; Nielsen et al., 2009). However, up to now, very few studies have been published on using thermally pretreated biomass in the pelletizing process (Gilbert et al., 2009; Lam et al., 2011), especially on the impact of torrefaction severity of the biomass on the pellet quality and integrity (Stelte et al., 2011c).

Although torrefaction is one of the promising methods for upgrading biomass feedstock, this technology requires the input of thermal energy and inert purge gases such as nitrogen (Yan et al., 2010). Currently, most of the published research about biomass torrefaction has focused on the compositional changes of solid biomass, along with the products distribution (Bridgeman et al., 2008; Medic et al., 2012). The volatiles released during torrefaction are also important. If the volatiles generated from the torrefaction can be burned in a combustor, then the combustion flue gases from the burner can be recycled and used for torrefaction and pre-drying, the torrefaction process may be self-sustained thermally with no need for additional thermal energy input and the inert gases, leading to considerable savings in both energy and inert gases and the process being economically viable. Up to know, although the composition of the volatiles generated from the torrefaction process is analysed (Bergman et al., 2005c), little has been done on whether torrefaction can be carried out properly in the presence of oxygen, because flue gases contain certain a few percentages of oxygen (Uemura et al., 2011; Rousset et al., 2012; Lu et al., 2011). Furthermore, whether torrefied biomass obtained in an oxidative torrefaction condition can be made into pellets of good quality is still in question.

In order to address the above problems, the main objectives of this study were to investigate the impact of oxidative torrefaction treatment on characteristics of torrefied sawdust and pellets. The oxygen concentration of the flue gases emitted from the fuel combustion process typically ranges from 2% to 6% (Haryanto and Hong, 2011; Tan et al., 2006), which can be taken as a reference for that of flue gases from combustion of torrefaction gases. In this study, the torrefaction of local softwood species was carried out in a thermogravimetric analyzer with a wide range of O_2 concentrations from 0% to 21% to study the oxidative torrefaction kinetics; whilst the simulated flue gases containing 0 to 6% oxygen was used to study the effect of oxygen level on torrefaction in a fluidized bed reactor. Torrefied sawdust was then compressed into pellets in a single die compression test unit. The making of torrefied pellets and properties of both torrefied sawdust and pellets, such as energy consumption during compression of torrefied pellets, pellet density, moisture uptake and Meyer hardness were then measured to identify suitable torrefaction and densification conditions, for making high quality and durable torrefied pellets, in comparison to traditional torrefied sawdust and pellets made from torrefaction without the presence of flue gas oxygen. The results from this work will provide knowledge not only related to the influence of process parameters (time and temperature) but also the effect of oxygen content of flue gases on the torrefied biomass and pellet properties.

2. Methods

2.1. Materials and analyses

The sawdust sample, obtained from RONA furniture store in Vancouver, is a mixture of spruce and fir, with spruce as the main component. The sample was separated into six size fractions, and 250–355 m is chosen for the fluidized bed reactor in this study. While pine particles of 0.23 mm in mean size were used in the TG experiment.

The high heating value (HHV) of the samples was measured with a Parr 6100 bomb calorimeter. The particle density was measured with a multipycnometer (Quantachrome Instruments). The ultimate analysis provides the composition of the biomass in wt.% of carbon, hydrogen and oxygen (the major components) as well as nitrogen, which were measured using Carlo Erba EA 1108 elemental analyzer (Thermo Scientific) in this study. Oxygen was estimated by the difference. Extractive contents were analysed using the dichloromethane (DCM) extraction method Tappi T204/Paptac G13. Results were calculated relative to sample weight on oven dry basis. While the method used for the Lignin analysis is according to NREL/TP-510–42618 (NREL, 2005).

The moisture absorption rates of raw and torrefied sawdust samples were measured in a humidity chamber (ESPEC CORP, LHU-113, Japan) at 30 °C at 90% relative humidity for 48 h. Before the test, all the samples were first dried in a convection oven at 103 °C for 24 h. The dry samples were then stored in a desiccator before use. The torrefied sawdust samples were kept inside the closed glass bottles. The samples inside the Petri dish were covered with a glass cap to prevent moisture loss when they were removed from the humidity chamber and weighted quickly using an ALC-80.4 analytical balance with 0.1 mg accuracy (Acculab, Edgewood, NY). The weight of the samples was measured every 20 min for the first four hours and every 60 min afterward.

As to all the measurement of the properties for both the untreated and torrefied biomass at different torrefaction conditions, two replicates were conducted, with the standard deviation being calculated.

2.2. TGA analysis

A TG analyzer, SHIMADZU TGA-50, was used to study the weight loss of biomass samples under various simulated flue gas oxygen content. Pine particles of 0.23 mm in mean size were used in the TG experiment. A sample of several (5–20) milligrammes for each TG experiment was put into a platinum sample cell, which was then located on a sample pan hanging inside a furnace tube under a N_2–O_2 gas mixture flow rate of 50 ml (STP)/min, with O_2 concentrations of 0%, 3%, 6%, 10% and 21%, respectively. The temperature refers to the temperature of the TGA furnace. The isothermal TG was conducted following such a procedure: (1) heating from the room temperature to 110 °C at a rate of 50 K/min, (2) holding at 110 °C for 10 min to have the sample dried, (3) heating up to the torrefaction temperature at a rate of 50 K/min, (4) holding at the torrefaction temperature for 10 h for torrefaction, (5) heating up to 800 °C at a rate of 50 K/min to complete the pyrolysis. To shorten the heating up time in the isothermal tests, a heating rate of 50 K/min was selected, which gave rise to less than 5% weight loss associated with the heating period. Three torrefaction temperatures were chosen for the isothermal experiments, i.e., 300, 280 and 260 °C.

2.3. Fluidized bed system and experimental procedure

The batch fluidized bed reactor is made of stainless steel, 1.5 m tall and 50 mm in diameter, as shown in Fig. 1. In the torrefaction tests, the sample of 250–355 μm was used to minimize the internal heat and mass transfer. In order to maintain stable fluidization during the hot test, a minimum operating gas velocity of $0.26\ m\ s^{-1}$ corresponding to a gas flow rate of $1.83\ m^3\ h^{-1}$, for sawdust load of 10 g was selected based on the cold model experiment, with details provided in an early publication from our group (Li et al., 2012a). First, with the sweeping flow of nitrogen, the

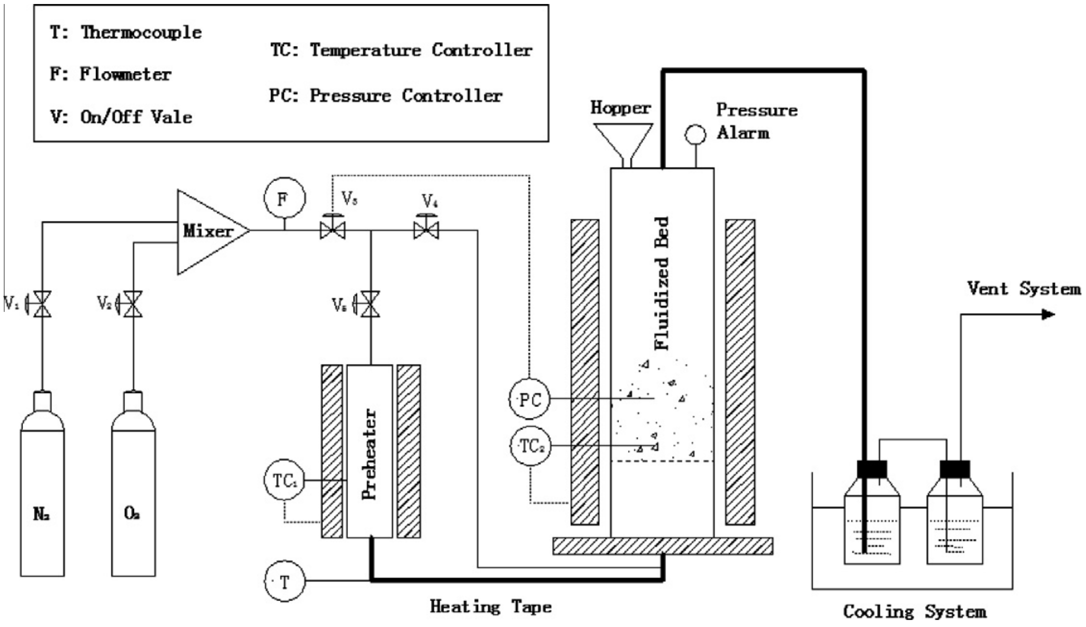


Fig. 1. Schematic of fluidized bed torrefaction unit.

preheater, the heating tape and the fluidized bed reactor were heated up to 650, 450 and 200 °C, respectively, and kept stable. Then the fluidized bed reactor was further heated up to the targeted torrefaction temperature slowly and kept stable for at least 10 min. The raw sample was added into the reactor from the top of the reactor, and the sweeping nitrogen gas was changed to the desired oxygen content. After torrefaction over the targeted residence time, the pre-heater and furnace heater were turned off to allow the unit cool down, followed by the cut-off of sweeping gas when the sample temperature dropped to below 200 °C. Finally, after the sample temperature decreased to the room temperature, the torrefied sample was discharged from the bottom of the reactor, completing the test.

The simulated flue gas was prepared from mixing nitrogen and oxygen from two separate cylinders. In this study, the concentration of oxygen in the sweeping gas varied from 0 to 6%, covering the typical range of oxygen concentration in combustion flue gases, with the test with 3% O_2 as the based case.

2.4. Pelletization tests and hardness measurement

A MTI 50 K (Measurement Technology Inc.) press with a heated single pellet die system was used to make one single pellet. The machine can be operated at various loading pressures to produce pellets of different density and size using both raw and torrefied sawdust, with the applied forces monitored by a load cell. The cylinder-piston unit was wrapped by a heating tape with a thermocouple and a temperature controller to maintain the inside cylinder to a desired temperature (also called die temperature). The piston diameter is 6.35 mm and 4000 N (compaction pressure of 126 MPa) pre-set load was used to compress the sawdust selected based on the preliminary test. The weight of the selected material for making one pellet was around 0.5 g. When the load force reaches 4000 N, the piston is held for 1 min. The energy consumptions associated with compaction and extrusion were obtained by integrating the force–displacement curve. To make control pellets, a die temperature of 70 °C is sufficient. However, according to the preliminary test result, torrefied samples prepared from both regular and oxidative treatment were difficult to be compressed into strong pellets under the same conditions as used for making the control pellets. So both untreated and torrefied pellets were also made by increasing the die temperature up to 170 °C for comparison. Other detailed description of the apparatus and operating procedures can be found in other two early publications from our group (Lam et al., 2012; Li et al., 2012b).

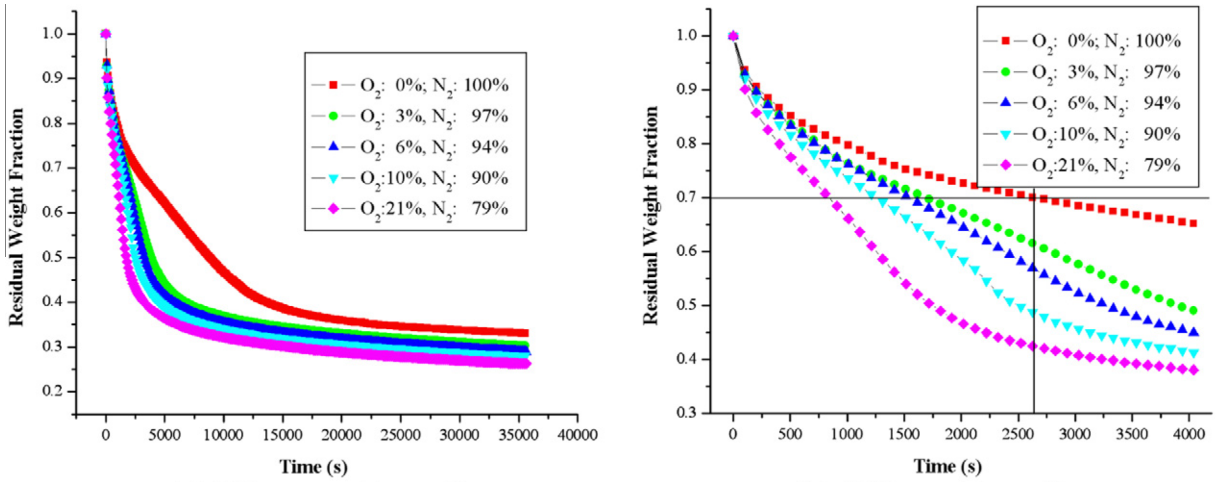
The MTI press machine was also used to measure the Meyer hardness of pellets, which reflects the resistance of the solid object to various kinds of permanent shape change when an axial force is applied. The parameters for hardness test were programmed and stored for the determination of a Meyer hardness using the Automated Materials Testing System software. Pellets of about 14 mm(±1 mm) in length and 6.5 mm in diameter placed on a plate horizontally. Compression tests were performed using a disc shaped metal probe with a ball bearing of 10 mm in diameter, the force is pressed in the middle of pellets' axial direction. The load was increased until the pellet ruptured. Three repeated tests were conducted for each sample.

3. Results and discussion

3.1. Torrefaction in a thermogravimetric analyzer

Fig. 2 shows the thermogravimetric curves of pine particles at different carrier gas oxygen levels at 280 °C. Table 1 shows the time to reach 30% mass loss, a typical target value for biomass torrefaction, the mass loss at 2644 s, and the weight fraction of final residual. Fig. 2(b) shows that the oxygen level in the carrier gas affected the mass loss characteristics significantly. The residence time required for achieving 30% mass loss at 3% oxygen concentration was 1690 s, much less than the 2640 s at 0% oxygen concentration. The final residual weight fractions or char yields in Fig. 2(a) were very generally lower at higher oxygen contents.

The implication from the TG test is that the presence of small amount oxygen will accelerate the degradation of those easily degradable components in the biomass at a given torrefaction temperature. This is likely related to the oxidation of unstable component of biomass (mostly hemicelluloses), in parallel with the thermal cracking in the absence of oxygen. However, the performance is insensitive to oxygen when the flue gas oxygen content varies within a certain range, e.g., 3 to 6% which is the typical



(a) 10 hours residence time

(b) 4000 s residence time

Fig. 2. TG curves of pine particles using carrier gas at different oxygen concentrations.

Table 1
Some important parameters for torrefaction with the presence of oxygen.

	O_2 concentration in the reaction atmosphere (%)				
	0	3	6	10	21
Time for 30% mass loss (s)	2640	1690	1540	1260	840
Mass loss at 2640 s (%)	30.0	38.6	43.2	51.4	57.6
Final residual weight fraction	0.331	0.303	0.290	0.281	0.263

oxygen content of combustion flue gases. The advantage of the use of oxygen-containing flue gases is the shortened torrefaction time and the less demand in energy input into the torrefaction reactor because of the heat release from the increased oxidation reaction between biomass and flue gas oxygen (Yan et al., 2010).

Our group (Peng et al. 2012) developed a two-component reaction kinetic model for torrefaction within short residence time with the weight loss less than 40% as below:

$$\text{Wood}_{\text{Fast Reaction Group}} \xrightarrow{k_1} \text{Volatiles} + \text{Chars} \tag{1}$$

$$\text{Wood}_{\text{Medium Fast Reaction Group}} \xrightarrow{k_2} \text{Volatiles} + \text{Chars} \tag{2}$$

where k_1 and k_2 are the global reaction rates of the fast reaction group and the medium reaction group, respectively. The fast reaction group may represent the decomposition of hemicelluloses; the medium reaction group accounts for the decomposition of cellulose and lignin. If the two overall reactions are assumed to be first order reactions, the residual weight fraction (W_{TGA}) of wood samples is given by:

$$W_{\text{TGA}} = (1 - C_1 - C_2) + C_1 \times \exp(-k_1 t) + C_2 \times \exp(-k_2 t) \tag{3}$$

where C_1 may be set as the fractional hemicelluloses content of biomass, C_2 represents the combined fractional cellulose and lignin contents of biomass.

By dividing the biomass into two reactive components and assuming that the oxidative torrefaction consists of two parallel reactions (Uemura et al. 2011), with one representing torrefaction and the other for oxidation, the following kinetic equations can be derived:

$$-r_{\text{overall}} = (-r_{\text{torrefaction}}) + (-r_{\text{oxiation}}) \tag{4}$$

$$-r_{\text{torrefaction}} = (-r_{\text{fast group torrefaction}}) + (-r_{\text{medium group torrefaction}}) \tag{5}$$

$$-r_{\text{oxidation}} = (-r_{\text{fast group oxidation}}) + (-r_{\text{medium group oxidation}}) \tag{6}$$

$$r_{\text{fast group torrefaction}} = \frac{dr_{\text{fast group torrefaction}}}{dt} = -k_1 \times C_{\text{fast group}}. \tag{7}$$

$$r_{\text{medium group torrefaction}} = \frac{dr_{\text{medium group torrefaction}}}{dt} = -k_2 \times C_{\text{medium group}}. \tag{8}$$

$$\begin{aligned} r_{\text{fast group oxidation}} &= \frac{dr_{\text{fast group oxidation}}}{dt} = -k'_{O1} \times C^{m1}_{\text{fast group}} \times C^{n1}_{O_2} \\ &= -k_{O1} \times C^{m1}_{\text{fast group}} \times y^{n1}_{O_2}. \end{aligned} \tag{9}$$

$$\begin{aligned} r_{\text{medium group oxidation}} &= \frac{dr_{\text{medium group oxidation}}}{dt} = -k'_{O2} \times C^{m2}_{\text{medium group}} \times C^{n2}_{O_2} \\ &= -k_{O2} \times C^{m2}_{\text{medium group}} \times y^{n2}_{O_2}. \end{aligned} \tag{10}$$

$C_{\text{fast group}}$ is the fast reaction group weight fraction, $C_{\text{medium group}}$ is the medium reaction group weight fraction, y_{O2} is the oxygen mole fraction, k_{O1} (= $k'_{O1}C^{n1}_{o}$) is the lumped oxidation reaction rate constant of the fast reaction group, k_{O2} (= $k'_{O2}C^{n2}_{o}$) is the lumped oxidation reaction rate constant of the medium reaction group, $m1$ and $m2$ are the oxidation reaction order for the fast reaction group and the medium reaction group, and $n1$ and $n2$ are the oxygen reaction order for the fast reaction group and the medium reaction group, respectively.

If the two oxidation reactions are assumed to be first order reactions with respect to the biomass concentration and the oxygen is in excess amount in the TG test, the residual weight fraction (WTGA) of softwood samples is given by:

$$\begin{aligned} W_{\text{TGA}} = (1 - C_1 - C_2) + C_1 \times \exp[-k_1 + k_{O1} \times y^{n1}_{O2})t] + C_2 \\ \times \exp[-(k_2 + k_{O2} \times y^{n2}_{O2})t]. \end{aligned} \tag{11}$$

The reaction rates for Eq. (11) can be defined as:

$$k_1 = A_1 e^{-\frac{E_1}{RT}} \tag{12}$$

Table 2
Two-component torrefaction and oxidation model reaction constants.

	Kinetics parameters	Fast reaction group	Medium reaction group
Torrefaction kinetic constants	E_1 (kJ mol^{-1})	145.9	168.6
	$\ln(A_1)$ (s^{-1})	24.71	26.17
Oxidation kinetic constants	E_{O1} (kJ mol^{-1})	86.62	153.4
	$\ln(A_{O1})$ (s^{-1})	13.11	25.86
	$n1$	1.0	0.69

$$k_2 = A_2 e^{-\frac{E_2}{RT}} \tag{13}$$

$$k_{O1} = A_{O1} e^{-\frac{E_{O1}}{RT}} \tag{14}$$

$$k_{O2} = A_{O2} e^{-\frac{E_{O2}}{RT}} \tag{15}$$

where E_1 and A_1 are the torrefaction reaction kinetics constants of the fast reaction group without oxygen. E_2 and A_2 represent the torrefaction reaction kinetics constants of the medium reaction group without oxygen. E_{O1} and A_{O1} are the oxidation reaction kinetics constants the fast reaction group. E_{O2} and A_{O2} represent the kinetics constants of the medium reaction group.

By linear regression of the experimental data in Fig. 2 and the corresponding data for the torrefaction temperatures of 260 and 300 °C over the range of approximately 0–40% weight loss against equation (11) using the least square fitting method, the reaction kinetic constants of the two-component torrefaction and oxidation model, E_1, E_2, A_1, A_2 E_{O1}, A_{O1}, E_{O2}, A_{O2} were estimated and summarized in Table 2.

It can be seen from Table 2 that the activation energy (E) for oxidation of fast reaction group is the smallest, followed by that of torrefaction of fast reaction group; the activation energy (E) for oxidation and torrefaction of medium reaction group increases gradually. The result indicates that oxidation reaction is less sensitive to the temperature than torrefaction reaction. The higher reaction order of the fast reaction group on oxygen ($n1$) indicates that the oxidation of hemicelluloses is more sensitive to the oxygen concentration.

To verify the kinetic model, experimental and fitted curves of 0.23 mm BC pine samples with different oxygen concentrations were compared in Fig. 3. It can be seen that the two-component torrefaction and oxidation model gave a reasonably good fit to the isothermal TG experimental data, especially at the high oxygen concentrations over the short residence time range at a weight loss of 0–40%, typical for torrefaction operation.

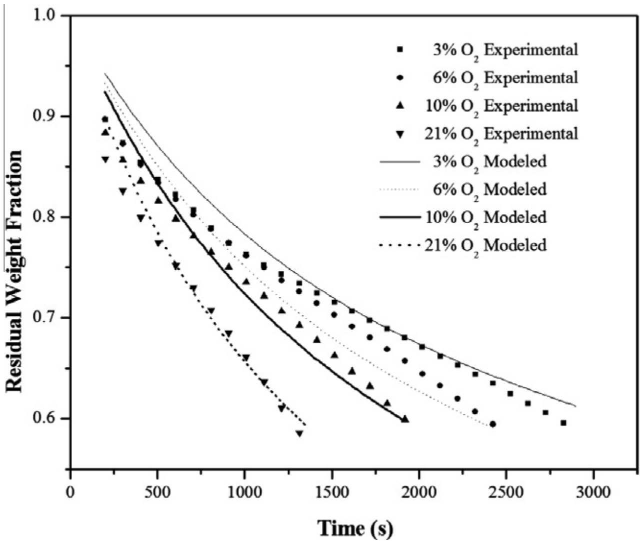


Fig. 3. Comparison of experimental and fitted TG curves for the residual weight fraction of 0.23 mm pine particles at 280 °C.

Table 3
Chosen torrefaction conditions for pelletization.

No.	Torrefaction temperature (°C)	Residence time (min)	O_2 concentration (%)	Weight loss (%)
1	250	42	3	30
2	270	25	3	31.5
3	270	24	3	29.8
4	290	4	3	30
5	290	7	3	36
6	270	12	6	31
7	270	30	0	36

3.2. Fluidized bed torrefaction and properties of torrefied sawdust

Our previous research (Li et al., 2012b)showed that pellets produced from the torrefied sawdust with around 30 wt.% weight loss had a higher hardness than those with less or higher than 30 wt.% weight loss. As a result, we targeted 30 wt.% weight loss for torrefaction to evaluate the effect of oxygen content in the carrier gas on the qualities of torrefied sawdust and pellets. Based on the TGA test results, it is seen that the sawdust lost its weight fast in the presence of oxygen in the carrier gas due to the contribution of gas phase oxygen to the oxidation of biomass. The torrefaction temperature and residence time for each run was selected based on the TG test results. The specific test conditions are given in Table 3.

Table 4 presents the results from the ultimate analysis of torrefied and untreated feedstock. When the traditional torrefied biomass (sample 7) is compared with the dry raw material, the elemental carbon content of torrefied biomass increased, but hydrogen and oxygen contents of torrefied biomass decreased, resulting in decreased H/C and O/C ratios. This may be due to the release of volatiles rich in hydrogen and oxygen, such as water and carbon dioxide. Lower hydrogen and oxygen contents of torrefied biomass are also associated with reduction in hydroxyl (OH) groups during torrefaction. Similar observations were also reported (Medic et al., 2012; Phanphanich and Mani, 2011). Similar trends were found for oxidative torrefied biomass in comparison to the untreated raw biomass.

When the oxidative torrefied biomass (samples 1–6) is compared with the regular torrefied biomass (sample 7), there is very little difference in their elemental contents. This may be due to the fact that oxidative torrefaction is a complex combined process of devolatilization, carbonization and oxidation, in which torrefaction and oxidation undergo in parallel and do not interact with each other (Uemura et al., 2011). At the same weight loss, the increase of oxygen concentration in the carrier gases imposed little effect on the HHV of torrefied sawdust, consistent with the results reported by other researchers (Uemura et al., 2011). In addition, to investigate the effect of oxidative torrefaction treatment on the product properties, Table 4 compares the dichloromethane (DCM) extractives and lignin content of dry raw material and three torrefied samples under 0%, 3% and 6% flue gas O_2 concentrations at the same temperature. It can be found that torrefaction decreased the extractives, but increased the relative lignin content compared with untreated biomass. Besides, oxidative torrefied samples had a slightly higher lignin content than normally torrefied samples. The DCM-extractable content of biomass is a measure of substances such as waxes, fats, resins, photosterols and non-volatile hydrocarbons. It is likely that most of the extractives are removed during

Table 4
Chemical composition analysis of torrefied and untreated feedstock.

No.	Torrefaction conditions	N (%)	C (%)	H (%)	O (%)	DCM extractives (%)	Lignin content (%)
0	Dry raw material	1.79 ± 0.13	46.52 ± 0.11	6.22 ± 0.01	45.48 ± 0.04	2.07	30.2
1	250 °C, 42 min, 3%O_2; 30 wt.%	0.33 ± 0.03	50.45 ± 0.07	5.26 ± 0.04	43.96 ± 0.06		
2	270 °C, 25 min, 3%O_2; 31.5 wt.%	0.39 ± 0.01	51.75 ± 0.49	5.51 ± 0.03	42.36 ± 0.01	0.063	53.3
3	270 °C, 24 min, 3%O_2; 29.8 wt.%	0.34 ± 0.11	51.32 ± 0.22	5.56 ± 0.13	42.80 ± 0.19		
4	290 °C, 4 min, 3% O_2; 30 wt.%	0.37 ± 0.04	51.59 ± 0.34	5.5 ± 0.01	42.54 ± 0.37		
5	290 °C, 7 min, 3% O_2; 36 wt.%	0.46 ± 0.09	53.51 ± 0.04	5.41 ± 0.11	40.63 ± 0.16		
6	270 °C, 12 min, 6% O_2; 31 wt.%	0.28 ± 0.01	52.22 ± 0.12	5.54 ± 0.04	41.98 ± 0.09	0.11	47.5
7	270 °C, 30 min, 0% O_2; 36 wt.%	0.39 ± 0.02	52.14 ± 0.11	5.87 ± 0.02	41.61 ± 0.11	0.22	42.8

Table 5
Particle density, higher heating value (HHV) and energy yields of raw and torrefied sawdust samples.

No.	Torrefaction conditions	Particle density (kg/m^3)	Higher heating value (MJ/kg)	Energy yield (%)
0	Untreated dry sawdust	1441 ± 25	18.93	
1	250 °C, 42 min, 3% O_2; 30 wt.%	1525 ± 18	20.98 ± 0.03	77.56 ± 0.11
2	270 °C, 25 min, 3% O_2; 31.5 wt.%	1521 ± 33	20.80 ± 0.66	75.26 ± 2.37
3	270 °C, 24 min, 3% O_2; 29.8 wt.%	1522 ± 22	21.34 ± 0.52	79.15 ± 1.96
4	290 °C, 4 min, 3% O_2; 30 wt.%	1541 ± 31	21.21 ± 0.11	78.42 ± 0.41
5	290 °C, 7 min, 3% O_2; 36 wt.%	1562 ± 50	21.82 ± 0.09	73.76 ± 0.32
6	270 °C, 12 min, 6% O_2; 31 wt.%	1637 ± 31	21.04 ± 0.14	76.69 ± 0.51
7	270 °C, 30 min, 0% O_2; 36 wt.%	1449	21.31 ± 0.39	72.03 ± 1.34

the torrefaction process. The relative increase in the lignin content by torrefaction is likely due to the fact that lignin is relatively inactive during torrefaction compared with cellulose and hemicellulose (Chen and Kuo, 2011); whilst other studies attribute this trend to the volatilization of some of the carbohydrate fractions and the formation of acid-insoluble degradation products during torrefaction (Stelte et al., 2011b; Yan et al., 2009). The significance of both extractives and lignin contents for the pelletization of sawdust will be discussed in Section 3.3.

Measured particle densities of raw sawdust and selected torrefied sawdust samples are shown in Table 4. The torrefied sawdust tends to have higher particle density than raw sawdust, which may be due to the shrinkage of particles during torrefaction and/or the reduction in internal particle pores (Mani et al., 2004). On the other hand, oxidative torrefaction in the presence of flue gas O_2 increased the particle density compared with torrefied sawdust without the presence of any oxygen, likely due to the oxidation of more light hydrocarbons in the biomass.

The higher heating value (HHV) and energy yields over torrefaction of raw and torrefied sawdust are also summarized in Table 5. As expected, torrefaction increased the sawdust HHV markedly because of the removal of low carbon content hemicelluloses. At the same weight loss, the increase of oxygen concentration in the carrier gases during torrefaction imposed little effect on the HHV of torrefied sawdust, consistent with the results reported by other researchers (Uemura et al., 2011), who postulated that torrefaction and oxidation occurred in parallel during oxidative torrefaction, with the two reactions not interacting with each other. The energy yields were in the range of 75.2–79.2% for test runs with 30% weight loss and 72.0–73.8% for those with 36% weight loss, with no clear correlation with the level of O_2 in the carrier gas. It seems that the amount of oxygen added to the torrefaction reactor did not have an obvious effect on the energy yield of torrefied biomass. Therefore, the energy yield is essentially determined by the mass yield no matter whether or not O_2 is present in the carrier gas, which is consistent with recent results (Rousset et al., 2012; Lu et al., 2012). Table 5 also shows that the energy yield decreased with increasing the severity of torrefaction or the mass loss. Similar observation was also reported in the studies of other researchers (Bridgeman et al., 2008; Phanphanich and Mani, 2011).

3.3. Pelletization and properties of torrefied pellets

There are two energy consumption processes associated with pellet making. One is the compression of sawdust for pelletization, which accounts for the major energy consumption, and the other is from the extrusion of the pellets out of the die, with a much less energy being consumed.

The results in Table 6 demonstrate that more energy was consumed to make pellets from torrefied sawdust than the raw untreated sawdust at the same die temperature (170 °C) and compression force (4000 N). For torrefied sawdust prepared at different carrier gas oxygen contents, the energy consumption for compression and extrusion were very similar to those prepared without the presence of oxygen in the carrier gas. This may be due to the lack of water and low hemicelluloses content in the torrefied sawdust. Water acts as a plasticizer, lowering the softening temperature of the wood polymers; whilst hemicelluloses bind lignin and cellulose fibrils and provide flexibility in the plant cell wall (Stelte et al., 2011b). Their degradation embrittles wood, making it easier to be comminuted into small particles (Chen et al., 2011a; Stelte et al., 2011b; Yildiz et al., 2006). As a result, pelletization parameters such as the friction coefficient and Poisson ratio are likely to be affected, leading to increased energy consumption (Chen et al., 2011a; Stelte et al., 2011b). Besides, extractives have been shown to play an important role during the densification process and are likely to act as the lubricant to lower the friction between the pellet and the metal wall (Stelte et al., 2011c). As the extractives in torrefied sawdust are decreased, higher energy consumption is expected during densification. The oxidative torrefaction at O_2 less than 6% did not change the properties of torrefied sawdust compared to regular torrefaction in the absence of O_2, leading to similar energy consumption associated with pelletization. The energy consumed for compressing torrefied sawdust at a die temperature of 170 °C, however, is lower than that of the raw untreated sawdust at a die temperature of 70 °C. This is mostly due to that lignin acts as a binding agent, which softens at elevated temperatures and helps the binding process (Kaliyan and Morey, 2009), consequently leading to less energy consumption.

The Meyer hardness of prepared pellets was obtained from the stress–strain curve from the crushing tests, following the proce-

Table 6
Energy consumptions associated with compression and extrusion of pellets, Meyer hardness, saturated moisture absorption of pellets, the pellet density before and after moisture uptake.

No.	Torrefaction conditions	Compression energy (kJ/kg)	Extrusion energy (kJ/kg)	Hardness (N/mm^2)	Moisture absorption (%)	Pellet density[a] (kg/m^3)	Pellet density[b] (kg/m^3)
0	Dry raw material (170 °C)	17.69 ± 2.39	0.195 ± 0.09	5.04 ± 1.79	13.78 ± 3.55	1098 ± 53	578 ± 48
0	Dry raw material (70 °C)	36.40	0.125	1.44	20.47	1050	501
1	250 °C, 42 min, 3% O_2; 30% (170 °C)	26.28	0.490	2.81 ± 0.84	11.06 ± 1.63	953 ± 33.4	723 ± 7.7
2	270 °C, 25 min, 3% O_2; 31.5% (170 °C)	27.06 ± 1.00	0.443 ± 0.034	2.39 ± 0.61	13.10 ± 2.73	971 ± 16.5	693 ± 10
3	270 °C, 24 min, 3% O_2; 29.8% (170 °C)	25.68 ± 0.74	0.308 ± 0.170	2.10 ± 0.59	13.26 ± 3.31	990 ± 10.7	694 ± 29
4	290 °C, 4 min, 3% O_2; 30% (170 °C)	26.57 ± 1.19	0.325 ± 0.070	2.38 ± 0.17	14.21 ± 6.86	965 ± 17.2	680 ± 16
5	290 °C, 7 min, 3% O_2; 36% (170 °C)	29.50 ± 1.96	0.354 ± 0.160	2.64 ± 0.52	12.85 ± 5.16	951 ± 47.8	651 ± 69
6	270 °C, 12 min, 6% O_2; 31% (170 °C)	28.46 ± 1.28	0.209 ± 0.144	2.10 ± 0.58	15.65 ± 3.56	958 ± 26.6	681 ± 30
7	270 °C, 30 min, 0% O_2; 36% (170 °C)	27.15 ± 0.13	0.272 ± 0.031	2.97 ± 0.55	9.03 ± 1.96	992 ± 29.9	757 ± 3.7

[a] Pellet density before moisture uptake.
[b] Pellet density after moisture uptake.

dures as mentioned in the literature (Doyle and Walker, 1985; Lam et al., 2012; Tabi et al., 2002). As shown in Table 6, the Meyer Hardness of torrefied pellets is generally lower than the control pellets made from raw sawdust under the same die temperature of 170 °C and a compression force of 4000 N, which is consistent with the results reported by other researchers (Stelte et al., 2011b). This may be due to that during torrefaction the amount of available hydrogen bonding sites is reduced, so that the strength of torrefied pellets is lowered compared to pellets made from untreated sawdust. Besides, the moisture content of the torrefied sawdust is lower, which results in an increase in the glass transition temperatures of the remaining hemicelluloses and lignin (Stelte et al., 2011a). Stelte et al. thus postulated that torrefaction may reduce the inter-diffusion of the wood polymers between adjacent particles in a pellet and thus the formation of solid bridges between them. The resulting pellets are more brittle than pellets made from untreated sawdust. However, the Meyer hardness of all torrefied pellets is higher than the control pellets prepared with a die temperature of 70 °C (1.44 N/mm^2), which is the temperature commonly used in making regular untreated wood pellets, confirming that torrefied pellets as strong as regular pellets can be produced at the expenses of a higher die temperature and higher compression energy consumption. Table 6 further shows that with the increase of oxygen content in the carrier gas for torrefaction, the Meyer hardness became slightly lower, which may be due to the oxidative removal of lignin, an important binding agent, from the biomass.

The hydrophobilicity of prepared pellets was examined in a humidity chamber. The saturated moisture content was obtained after exposing the pellets to the moist air at 30 °C and 90% relative humidity for 48 h inside the humidity chamber. As shown in Table 4, all torrefied pellets have a higher hydrophobicity than untreated control pellets, which may be due to the loss of hydroxyl (OH) groups from biomass during torrefaction (Phanphanich and Mani, 2011; Pimchuai et al., 2010).

For pellets prepared at a die temperature of 170 °C, the control pellet also improved the hydrophobicity largely likely because of the thermal modification of pellet surface during higher temperature compaction and extrusion. For those pellets produced from torrefaction using the carrier gas containing oxygen, their hydrophobicity was reduced. This may be due to the higher content of hydroxyl group in the oxidative torrefied particles or the increased pore volume or surface area, which needs to be investigated further in the future. The density of prepared regular and torrefied pellets before and after water uptake was measured by a multipycnometer, and shown in Table 6. Comparing samples 0–7 prepared in this study at the same die temperature of 170 °C, it is seen that before moisture absorption, the density of torrefied pellets is about 10% lower than the control pellet made from raw sawdust (run 0). This is mainly due to the formation of more inter-particle gaps and voids by torrefaction, which leads to a lower pellet density. However, all torrefied biomass pellets have a similar density, insensitive to the oxygen content used in the preparation of torrefied sawdust. While after moisture absorption, the pellet density decreased from about 1–0.7 for torrefied pellets. But for control pellet, its density decreased from 1 to 0.58/0.501 for the condition of die temperature of 170 and 70 °C respectively, indicating that a more significant expansion in the volume after water uptake than torrefied pellets. As a result, the hydrophobilicity of torrefied pellets will have an advantage over the control pellet from the pellet handling logistics point of view.

4. Conclusions

Oxidative torrefaction of sawdust was investigated in a fluidized bed reactor, then made into dense and strong pellets of high hydrophobicity, with similar properties to normally torrefied sawdust and corresponding pellets, especially on the density, energy consumption for pelletization, higher heating value and energy yield. A two-component reaction kinetic model for oxidative torrefaction was developed based on TGA analysis, which fits well to the isothermal TGA experimental data. Therefore, from the process integration and cost point of view, it is feasible to use oxygen laden combustion flue gases as the carrier gas for torrefaction of biomass.

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